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Hydrothermal synthesis and characterization of cobalt (III) hydrated pyrophosphate crystals: $2(CoHP_2O_7)$

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Abstract $2(CoHP_2O_7)$ crystals were synthesized by hydrothermal technique in the form of single crystals and characterized by DTA, FTIR and X ray diffraction method. $2(CoHP_2O_7)$ crystals crystallized in monoclinic systems with cell parameter of a = 9.1609, b = 12.6764, c = 9.6868 Å, $\alpha = \gamma = 90°$, β = 106.7705°, v = 1077.06 (15) Å^3 with space group $P2_1/C_1$ and paramagnetic nature. Solubility studies indicate that this compound shows positive coefficient of solubility.

Keywords : Hydrothermal synthesis, pyrophosphates, FTIR, magnetism and solubility.

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1. Introduction

Phosphates were studied extensively owing to there wide range of applications such as piezoelectric, luminescence, ceramics, superionics, magnetic, *etc* [1-5]. Subsequently, there are also reports on pyrophosphates exhibiting simple framework structure with relatively high ionic conductivity values [6,7]. These pyrophosphates are much easier to obtain in the form of single crystals by hydrothermal techniques. Here, we report a new group of polymerized pyrophosphate, which exhibits framework type of structure with paramagnetic nature at ambient condition.

2. Experimental

$2(CoHP_2O_7)$ crystals were synthesized by the hydrothermal processing. The growth of phosphates by the hydrothermal technique is quite complicated, because of high corrosive and volatile nature of phosphorus at elevated temperature [8]. Adopting earlier methods, the present experiments were carried out in Morey type autoclaves provided with Teflon liners (Figure 1), at the temperature range of 230 – 265°C and pressure of 60-100 bars respectively [9]. All reagents used in the synthesis process were of Analar grade with 99.9 % purity from Merck. Desired quantity of $CoCl_3$ was dissolved in of 85% H_3PO_4 and was taken in Teflon liners. The crystallization was carried out by spontaneous nucleation controlled through a slow and programmed rate of heating. The authors were able to

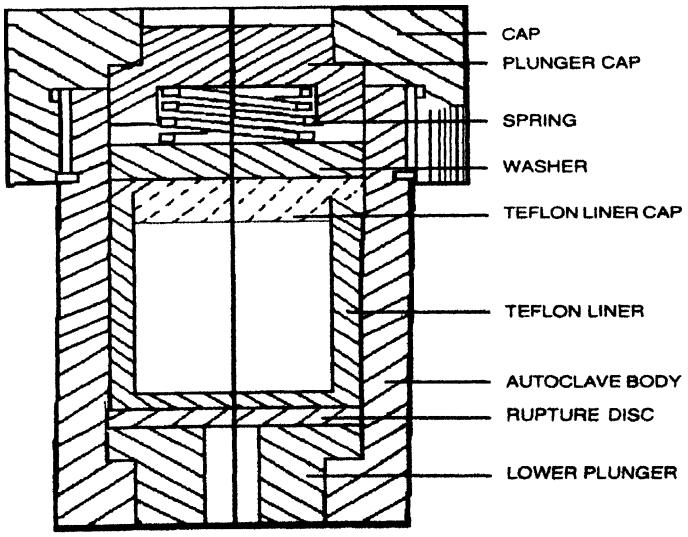

Figure 1. Schematic diagram of Morey type autoclave.

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synthesized $2(CoHP_2O_7)$ crystals under the following experimental conditions:

Molar ratio $= Co_2O: P_2O_5 : H_2O$

$1 - 1.5: 10 - 12: 8 - 10$

T= 260°C; P = 80 bars; Duration= 8 days.

The following reactions could explain the formation of $2(CoHP_2O_7)$;

$$2CoCl_3 + 2H_3PO_4 \rightarrow Co_2(PO_4)_2 + 6HCl, \quad (1)$$

$$Co_2(PO_4)_2 + 2H_3PO_4 \rightarrow 2(CoHP_2O_7) + H_2O \quad (2)$$

On the whole, $2(CoHP_2O_7)$ crystals obtained were of good quality and exhibit well-developed morphology with smooth surface, pink colour and translucent luster. The size of the crystals is 0.5 to 3 mm (Figure 2). The growth along the basal planes is much faster than along the other faces.

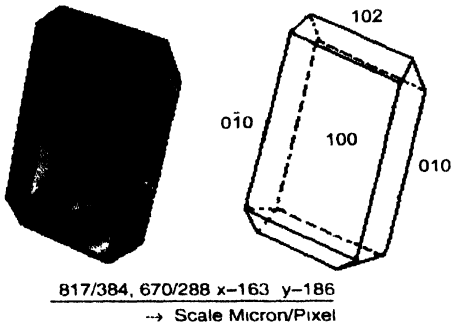

Figure 2. Photograph of $2(CoHP_2O_7)$ crystal and schematic diagram.

Solubility study :

Solubility study is an impotent parameter for the successful growth of phosphates in the form of single crystals. The lack of systematic studies of solubility data was responsible for the earlier failures in the growth of phosphates by hydrothermal methods [10]. Chengqian Zhang *et al* attributed that based on the solubility results of a compound it is possible to optimize the growth conditions [11]. The solubility measurements were carried out by weight loss method to understand the growth process and to optimize the growth conditions. Here, a crystal is kept in equilibrium at the desired pressure and temperature conditions for a known period in various normality of H_3PO_4 solution. The solvent - solute interaction has been studied in detail with reference to the temperature and normality of H_3PO_4. The results indicate positive correlation of solubility with both normality and temperature ranging from 0.085 to 0.125gl-1T-1. However, maximum percent of solubility observed at the temperature range of 250-275°C in various normality of H_3PO_4 solutions (Figure 3). Based on these results, it was possible to optimize the growth temperature of the studied compound (250 -260°C).

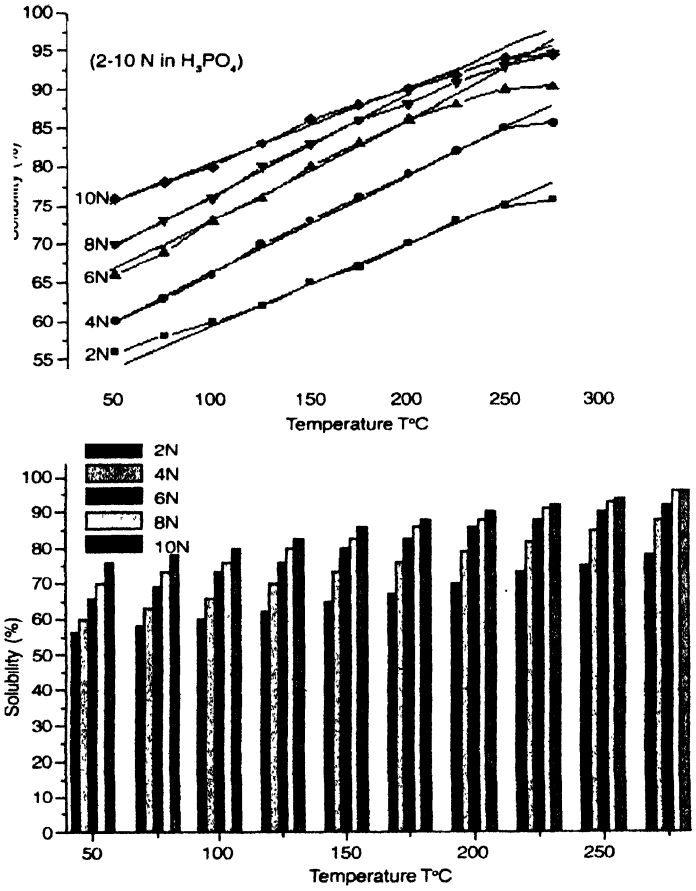

Figure 3. Solubility curve of $2(CoHP_2O_7)$ compound and histogram.

FTIR spectroscopy :

FTIR spectrum recorded by a high resolution Perkin Elmer Infrared Spectrophotometer in the range of 4000- 400 cm^{-1} (Figure 4). This compound exhibits number of prominent fine and splitting absorption bands especially in the four frequency regions *i.e.* at $\nu_1 = 3330\ cm^{-1}$, $\nu_2 = 2144 - 1600 cm^{-1}$, $\nu_3 = 1165 - 930 cm^{-1}$ and $\nu_4 = 723 - 480\ cm^{-1}$ regions. The most interesting feature of this spectrum is the presence of H-O-H molecule, which is clearly depicted in the region 3330 cm^{-1}. The vibrational band at 2144 –1600 cm^{-1} is due to the presence of cobalt bearing molecules. Higher the degree of condensation, there will be higher degree of complexity and splitting in the IR spectra of phosphates [12]. Vibrations at 1165 – 930cm^{-1} and 723 – 480 cm^{-1} regions exhibit fineness and multiple splitting, which clearly indicate the stretching of P – O – P molecules and the condensation of $[PO_4]^{3-}$ tetrahedra to $[P_2O_7]$.

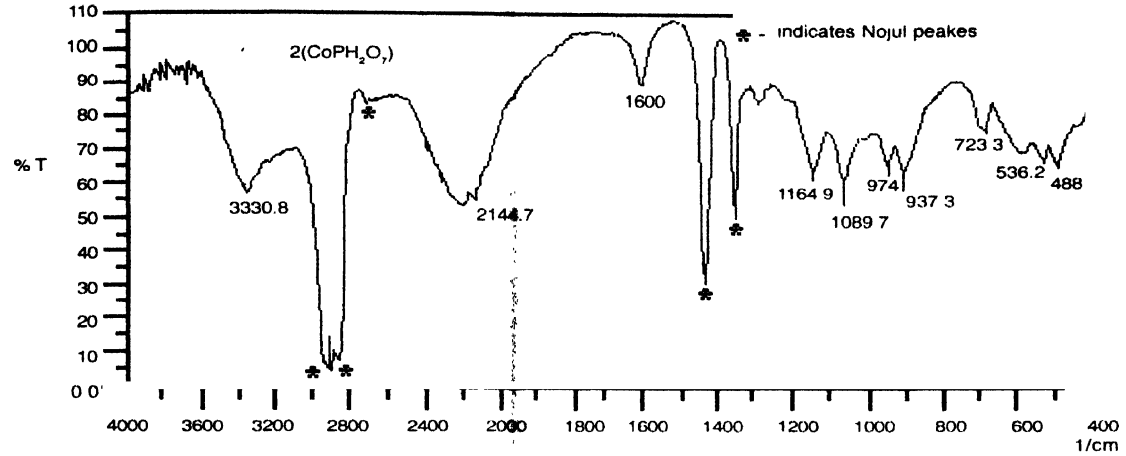

Figure 4. FTIR spectrum of $2(CoHP_2O_7)$ compound

Differential thermal analysis :

The DTA curve was recorded using DTA/ETA instrument (Model 021 NAL India) from room temperature to 600°C. The results yielded multiple endothermic peaks (Figure 5). The peak at 128°C is due to liberation of water molecule and the peak at 235°C is due to the chemical diffusion. Subsequently, the compound started melting at 400°C and clearly indicates low thermal stability compared to the derivative of alkali pyrophosphates reported earlier [9].

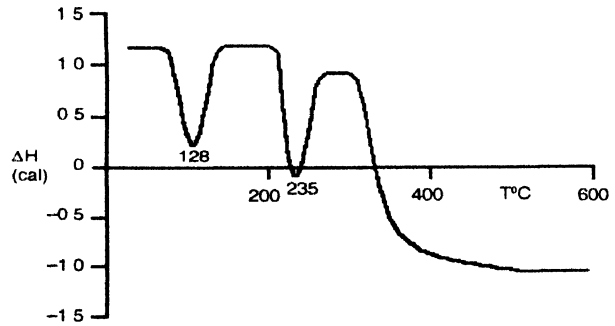

Figure 5. DTA curve of $2(CoHP_2O_7)$ compound

X-ray diffraction :

The X- ray diffraction study was carried out for single crystal of $2(CoHP_2O_7)$. The measurements were made on a DIPLabo Imaging Plate system with graphite monochromatered radiation (MoKα). Thirty-six sets of data were collected by oscillation method. The compound crystallized in monoclinic system and space group is $P2_1/C_1$ with cell parameters of $a = 9.1609$, $b = 12.6764$, $c = 9.6868$ Å, $\alpha = \gamma = 90°$, $\beta = 106.7705°$ and $v = 1077.06$ (15) Å^3. Structure was solved using SHELEX 97. The statistical weight factor was also included in the last cycle of refinement. ORTEP of the molecule with 50% probability is shown in (Figure 6). The polymerization of phosphates with Co has made as to reveal its coordinates and packing mode. Each Co atom has coordinates with six pyrophosphate oxygen atoms that is, from two O- atoms of one terminal pyrophosphate. Detailed structure is discussed elsewhere [13].

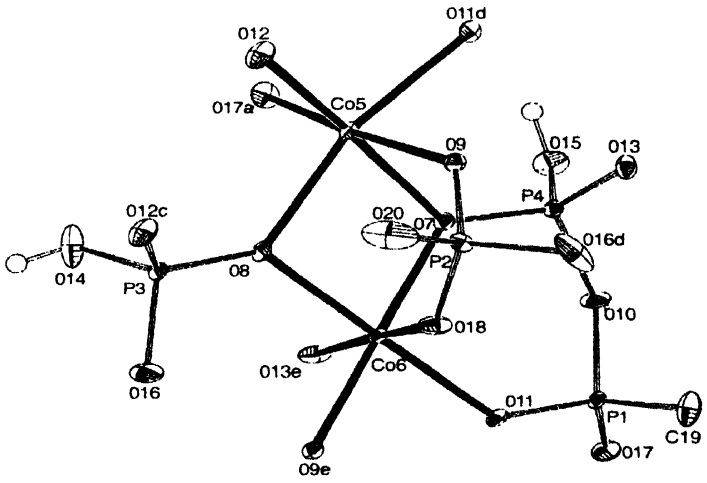

Figure 6. ORTEP diagram of $2(CoHP_2O_7)$ molecules at 50% probability.

Magnetic property :

Magnetic susceptibility measurements are made using Gouy's balance by applying field strength of 0.5 – 2.5 K Gauss at 300K. Magnetic moments of cobalt bearing compounds fall in two broad classes. First, those are having essentially temperature - independent magnetic moments due to mononuclear complexes having interaction between the unpaired electrons on different cobalt ions in the range of 4.3 – 5.2 BM. The second in which the moments are temperature dependent. The preliminary investigation of the compound exhibits magnetic moments in

the range from 2.79 – 3.98 BM (Figure 7) indicating paramagnetic nature. However, the values are relatively lower than the cobalt derivatives. Detailed investigations will be discussed elsewhere

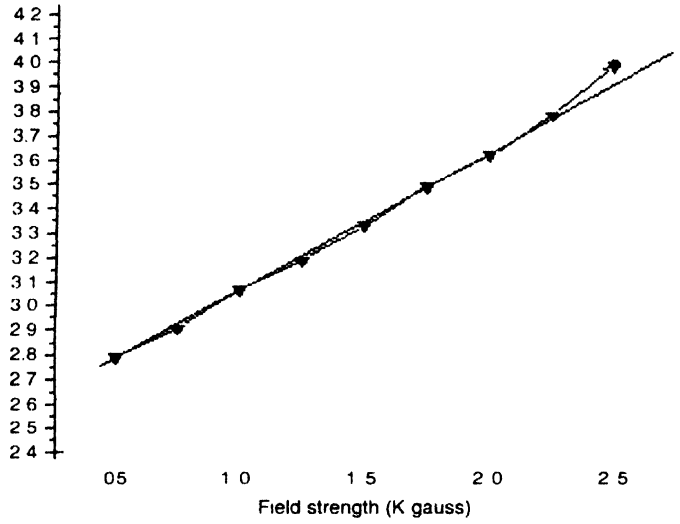

Figure 7. Magnetic moment of $2(CoHP_2O_7)$ compound

3. Conclusion

$2(CoHP_2O_7)$ crystals were synthesized by hydrothermal method in the form of single crystals with well-developed morphology. Solubility studies indicate that this compound shows positive coefficient of solubility. Single crystal X-ray studies revealed that this compound crystallized in monoclinic system with framework structure. Preliminary magnetic results indicate that to be a paramagnetic.

Acknowledgments

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